

PET COPROCESSING WITH YALLOURN BROWN COAL UNDER HYDROLIQUEFACTION CONDITIONS

G. D. Bongers, T. V. Verheyen, D. J. Allardice, and Toshiaki Okui*

HRL Technology Pty Ltd, Melbourne, Australia.

*New Energy and Industrial Technology Development Organisation, CCT Centre,
Tokyo, Japan.

KEYWORDS: Hydroliquefaction, PET, brown coal, coprocessing.

INTRODUCTION

Polymer feedstocks such as polyethylene terephthalate (PET) are all prepared from non-renewable fossil fuels such as natural gas and petroleum sources, and as such need to be responsibly managed to increase the life of these resources. Post consumer plastics represent an increasing problem in terms of their disposal with many Governments tightening controls on their dumping as waste and encouraging recycling via legislation. Coprocessing of waste polymer within a brown coal liquefaction plant offers an alternative disposal option for these wastes, a supplementary source of hydrogen and the potential to increase the hydrocarbon content the liquid products [1-5].

The objectives of this study were to evaluate the efficacy of PET coprocessing in regard to the first stage hydroliquefaction of Yallourn Eastfield brown coal. The investigation of the molecular coal-PET interactions was an integral component to evaluate the coprocessing mechanisms.

EXPERIMENTAL

Pyrolysis Gas chromatography mass spectrometry (PY GC/MS) analysis was conducted using chromatography conditions previously reported [6].

Liquefaction experiments were conducted under similar conditions to those used by others [7], except that the autoclaves agitated in the horizontal direction.

RESULTS AND DISCUSSION

PY GC/MS ANALYSIS OF POLYMER FEEDSTOCK

PY GC/MS of the virgin PET was conducted to characterise its thermal breakdown products in the absence of any interferences from coal, solvent or catalyst. The pyrograms obtained for the sequential 340, 450 and 720°C flash pyrolysis of the polymer is presented in Figure 1. Thermal cleavage produces the expected benzene, benzoic and dibenzoic acid products. Dimer and trimer sections of the original polymer dominate the PET pyrogram at 720°C.

PET melts but does not significantly decompose at 340°C or even 450°C under flash pyrolysis conditions as seen by a lack of peaks in Figure 1a & b. Pyrolysis is important from the coprocessing viewpoint as it implies that unless liquefaction conditions have some promoting effect, pyrolytic cleavage would occur only slowly at typical hydrogenation reaction temperatures (eg. 430°C). Competing effects of pressure, catalyst, solvent and reaction time during liquefaction make it difficult to predict its reactivity. However, it should be noted that PET is not going to simply fall apart during the reactor warm-up phase.

COPROCESSING WITH DIFFERENT PET LOADINGS

The yield data in Figure 2 suggests that PET addition is synergistic at very low levels and has a negative effect at higher loadings. Asphaltene yield appears unaffected by coprocessing and suggests negligible interaction between the coal and polymer at this level. PY GC/MS provides further information on the degree of interaction between coal and PET.

The pyrograms for the asphaltenes produced from both 100% coal and coal coprocessed with 1% PET under catalysed conditions (refer to Figure 3) reveal negligible differences in the type and distribution of the compounds released. Coprocessing with 10% PET

results in the asphaltenes incorporating additional toluene and C2 benzene's. Very few aromatic acids are present in the asphaltenes with benzoic acid undetected and only a trace of its methyl derivatives, in contrast to neat PET.

At a 50% PET loading, the pyrogram of the coprocessed asphaltene product contains proportionately more toluene and xylenes but is again devoid of acidic PET fragments. 100% PET when subjected to catalysed hydrolifuefaction produces asphaltenes that are dominated by benzoic and methyl benzoic acids. The concentration of these acids is negligible in the asphaltenes produced under coprocessing conditions. Even the 50% PET coprocessing pyrogram includes negligible acids suggesting Yallourn coal promotes their decarboxylation to aromatic hydrocarbons, thus a better quality oil. Toluene and C2 benzenes are the dominant products in the 50% PET coprocessing pyrogram.

The pyrograms from the corresponding residue or insoluble hydrolifuefaction products reveal the expected increase in PET derived compounds with higher polymer coprocessing ratios. However, these pyrograms of coprocessed residues do reveal some more interesting features:

- a reduction in the coal derived alkene alkane ratio compared with 100% coal,
- different distribution and types of PET breakdown products in the asphaltenes,
- a lack of poly aromatic ketone species found in the 100% PET experiment.

The first observation lends support to synergism at low PET levels whilst the second is in accord with the differing origin of the two fractions. Solubility constraints imposed by THF would explain the structural differences between asphaltenes and residues. The absence of any larger PET derived fragments in the coprocessing residues suggests the coal either promotes their destruction or they may be incorporated into its macromolecular structure.

The PET present in the residue has been modified by the hydrolifuefaction conditions with a loss of the more complex benzoic acid derivatives present in the virgin polymer decomposition products (Figure 1). This means that the PET is not unreactive with its thermal cleavage products simply incorporated into the residue, instead it is being converted into an insoluble product which has less carboxyl groups and is more intractable. The coal-derived phenols are still discernable in the 50% coprocessing level pyrogram but the pyrogram is dominated by a number of partially hydrogenated PET derived compounds along with benzoic acid.

The fact that some carboxyl groups survive the hydrolifuefaction treatment indicates that these conditions are not as extreme as first thought. The compounds identified by PY GC/MS suggest PET may have the ability to become partially incorporated into the brown coal's structure. Some PET decomposition products may become chemically bound to the macromolecular structure of the insoluble coal products. Hydrolifuefaction of neat PET results in a residue that produces relatively little toluene on flash pyrolysis in contrast to the coprocessing experiments. The opposite is true for benzoic acid suggesting that the coal may be incorporating the benzoic acid hydrolifuefaction products within its insoluble product to be released as toluene on flash pyrolysis.

EFFECT OF TEMPERATURE ON PET COPROCESSING

Reducing the reaction temperature by 60°C to 370°C produced the expected reduction in conversion for Yallourn Eastfield coal. However, the effect when 10% PET was coprocessed was more marked with a decline of more than 10% in both conversion and asphaltene yield. These results suggest that the polymer is not only failing to contribute towards the coal conversion process at 370°C but is actually hindering it. This behavior is consistent with the polymer not dissolving and decomposing sufficiently at the lower temperature as shown in the pyroprobe work (refer to Figure 1). Pyroprobe experiments reveal that the PET is molten at this temperature under ambient pressure but shows little sign of decomposition. The polymer may swell reducing the supply of solvent and hydrogen available to react with the coal.

The asphaltene pyrograms in Figure 4 reveal that the long chain aliphatic hydrocarbons in the 370°C pyrogram are three times the size of those in the 430°C derived sample. This confirms that at the lower liquefaction temperatures these long chain aliphatic hydrocarbons are not formed or released from the coal into the oil fraction. The input from PET degradation products in terms of higher benzene and C2 benzenes becomes

more obvious with increasing temperature, however, these peaks are still proportionately larger in the 370°C pyrogram than they are for 100% coal.

The pyrograms from the residues reveal additional insights into the effect of lower reaction temperature on coprocessing at the molecular level. The pyrograms of the residues contrast those from the asphaltenes by their significant differences in the types and yields of peaks. The 370°C pyrogram has more coal related long chain aliphatics in accord with less severe processing leading to their retention in the residue.

Tetralin is released from this residue but not from the 430°C suggesting it may have been locked away from THF by incorporation within the PET. The residue produced under these milder conditions releases less benzoic acid and PET fragments than the 430°C. This suggests that the two PET derivatives present in the different residues are undergoing different pyrolytic fragmentation. It is not simply a case of better preservation of PET from the 370°C run as its products are not the same as those are for 100% PET as viewed in Figure 1. The PET derivative prepared at 370°C may contain sufficient solvent to undergo a separate copyrolysis leading to a different product distribution.

CONCLUSIONS

Coprocessing brown coal with PET has minimal impact on first stage hydroliquefaction at low PET loadings. Therefore hydroliquefaction is a possible beneficial disposal alternative for PET on an industrial scale.

The lower amounts of aromatic acids and higher alkyl benzenes produced on the flash pyrolysis of coprocessed products compared to 100% coal or polymer is evidence at the molecular level for the formation of coal/polymer compounds.

Solvent is absorbed into PET at low liquefaction reaction temperatures (370°C). At normal liquefaction temperatures (eg. 430°C) the polymer melts but does not readily decompose.

PET requires severe reaction conditions to completely decompose as evidenced by the residual benzoic acid released from the catalysed 430°C residue.

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ACKNOWLEDGEMENTS

Funding of this research project by New Energy and Industrial Technology Development Organisation (NEDO) via Nippon Brown Coal Liquefaction Co Ltd (NBCL), Japan, is gratefully acknowledged.

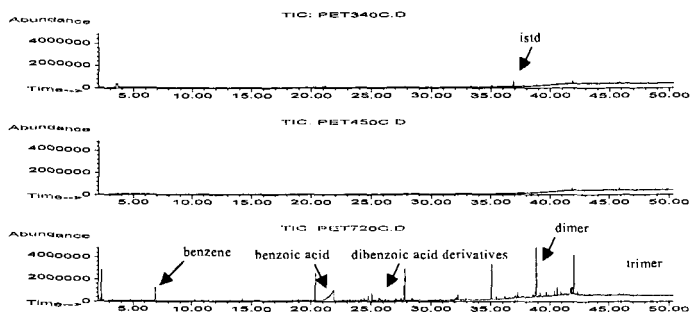


Figure 1. Pyrograms for PET revealing the minor loss of volatiles at the lower flash pyrolysis temperatures

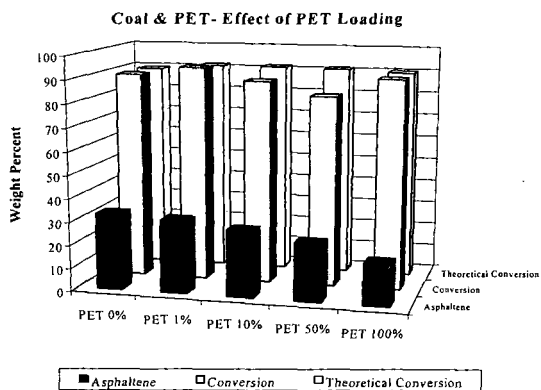


Figure2 Yield data covering the effect of coprocessing Yallourn Eastfield coal with PET at different polymer loadings.

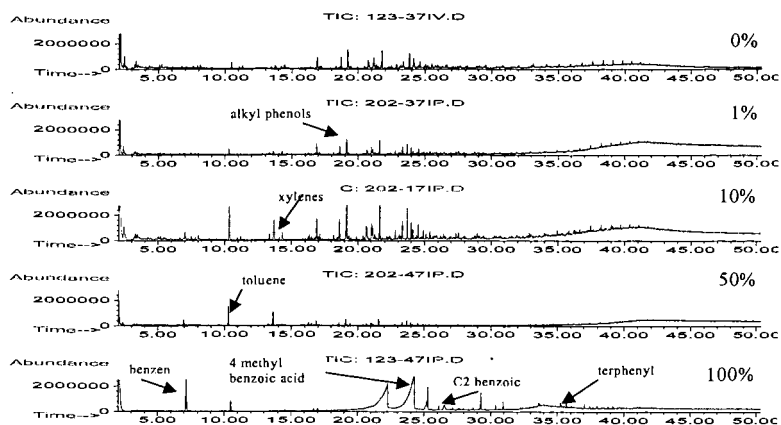


Figure 3 PY GC/MS pyrograms for asphaltenes from a PET profile: 0, 1, 10, 50 and 100% PET loading for catalysed coprocessing with Yallourn Eastfield coal.

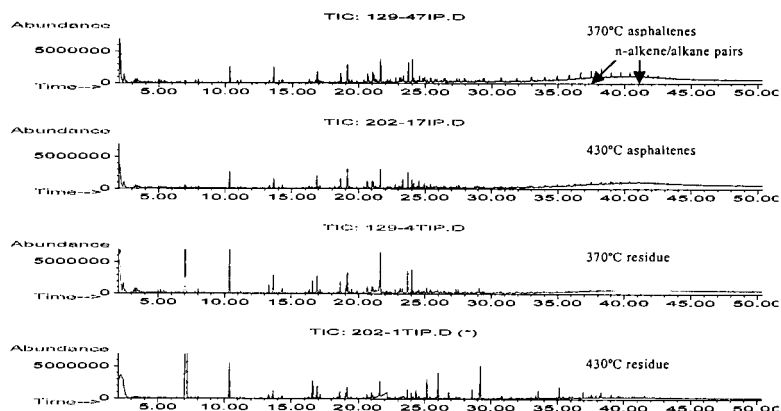


Figure 4 PYGC/MS chromatograms comparing the effect of 370°C vs 430°C liquefaction temperature on the asphaltene and residues